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Research Article

Synthesis, Crystal Structure, Catalytic Properties, and Luminescent of a Novel Eu(III) Complex Material with 4-Imidazolecarboxaldehyde-pyridine-2-carbohydrazone

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Abstract

A novel Eu(III) complex, $[Eu(L)_2(H_2O)_4]\cdot(NO_3)\cdot(H_2O)_4$ (**1**) (H_2L = 4-imidazolecarboxaldehyde-pyridine-2-carbohydrazide), was synthesized. Its structure has been characterized by elemental analysis, IR, and X-ray single crystal diffraction analysis. Complex **1** is of orthorhombic, space group *Fdd*2 with a = 29.471(6) A°, b = 10.287(2) A°, c = 24.340(5) A°, V = 7379(3) A°3, Z = 8, Mr = 902.58, Dc = 1.625 μg·m^{-3}, μ = 1.789 mm^{-1}, F(000) = 3656, $GOOF$ = 1.099, the final R = 0.0517, ωR = 0.1292 for 3043 observed reflections with $I > 2\sigma(I)$. The A3 coupling reaction has been investigated using the complex **1** as catalyst. The luminescent spectrum of the complex **1** gives two weak peaks (448 nm and 491 nm) and two strong peaks (596 nm and 620 nm) from excitation at 279 nm.

Keywords: Eu(III) complex; Luminescence; pyridine; carbohydrazone; Catalyst

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1. Introduction

Increasing studies have been focused on the europium complexes, because they show rich coordination model, biological activity, catalytic activity and strong red luminescence [1-4]. So far, various Eu(III) complexes with multipodal ligands, such as diketonate [5], Schiff-base [6], carboxylate [7], and bipyridyl [8] have been reported. Meanwhile, hydrazone compounds are excellent multipodal ligands [9], and their metal complexes have also shown good properties in cytotoxic activity [10], luminescence [11], and catalytic application [12]. Syntheses of propargylamines under heterogeneous catalysis are particularly attractive as they allow the production and ready separation of large quantities of products using small amounts of catalysts. So the development of heterogeneous catalysts for preparing propargylamines by the A3 coupling reaction remains an active research area [13-17]. However, so far, there is little research on the catalytic activity of Eu(III) complexes. As part of our research interest, in this paper, a novel Eu(III) complex was reported. Moreover,

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the synthesis, crystal structure, catalytic activity and luminescent property of Eu(III) complex have also been investigated. The scheme of 4-imidazolecarboxaldehyde-pyridine-2-carbohydrazide is given in Figure 1.

2. Materials and Method

2.1. Materials and measurements

4-Imidazolecarboxaldehyde (A. R.), pyridine-2-carbohydrazide (A.R.) and $Eu(NO_3)_3 \cdot 6H_2O$ (A.R.) were purchased from Aladdin Reagent Company. The analyses of C, H, and N were made on a Elementar Vario EL III elemental analyzer. Infrared spectra (KBr pellets, 4000-400 cm^{-1}) were recorded on a Nicolet NEXUS 670 spectrophotometer. The X-ray single-crystal data collection for complex **1** was performed on a Bruker Smart-1000 CCD diffractometer. The luminescent emission spectrum of complex **1** in solid state was measured on a PE LS-55 spectrometer.

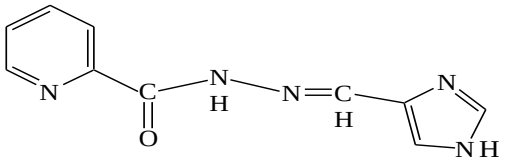

Figure 1. The scheme of H_2L

2.2. Synthesis of 4-imidazolecarboxaldehyde-pyridine-2-carbohydrazide

A mixture of 4-imidazolecarboxaldehyde (0.9609 g, 1.0 mmol) and pyridine-2-carbohydrazide (0.1371 g, 1.0 mmol) in 5 mL CH_3CH_2OH was refluxed for 6 h. The precipitate of 4-imidazolecarboxaldehyde-pyridine-2-carbohydrazide was filtered off and dried. Elemental analysis calc. for $C_{10}H_9N_5O$: C, 55.81, H, 4.19, N, 32.56 (%); Found: C, 55.62, H, 3.86, N, 32.83(%). IR: 3356 cm^{-1} (H_2O), 1662 cm^{-1} (C=O), 1652 cm^{-1} (C=N).

2.3. Synthesis of complex 1

The 4-Imidazolecarboxaldehyde-pyridine-2-carbohydrazide (0.430 g, 2.0 mmol) and $Eu(NO_3)_3 \cdot 6H_2O$ (0.4461 g, 1.0 mmol) were dissolved in 10 mL H_2O/CH_3CH_2OH (v:v=1:1). The solution mixture was heated at 50 ℃ for 6 h. The resultant solution was filtered and left

Table 1. The most crystal data of complex **1**

Empirical formula	$C_{20}H_{32}N_{11}O_{13}Eu$
Formula weight	786.50
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	FDD2
a/Å	29.471(6)
b/Å	10.287(2)
c/Å	24.340(5)
$\alpha = \beta = \gamma$ /°	90.00
Volume/Å^3	7379(3)
Z	8
ρ_{calc} mg/mm^3	1.625
μ/mm^{-1}	1.789
S	1.115
F(000)	3656
Index ranges	$-34 \le h \le 34$, $-11 \le k \le 11$, $-28 \le l \le 28$
Reflections collected	13511
Independent reflections	3214 [R(int) = 0.071]
Data/restraints/parameters	3214/6/236
Goodness-of-fit on F2	1.082
R_1, wR_2 [all data]	0.0531, 0.1306
R_1, wR_2 [$I>2\sigma(I)$]	0.0517, 0.1292

aside for crystallization at room temperature. The crystals appeared for 30 days which were collected by filtration. Elemental analysis calc. for $C_{20}H_{32}N_{11}O_{13}Eu$: C, 30.51, H, 4.07, N, 19.58 (%); Found: C, 30.32, H, 4.36, N, 19.81 (%). IR: 1622 cm^{-1} (C=O), 1619 cm^{-1} (C=N).

2.4. Crystal data and structure determination

X-ray diffraction analysis of complex **1** was carried out at 293 (2) K on a Bruker Smart-1000 CCD diffractometer by using a φ~ω scan mode. The structure was solved by direct methods with SHELXL-97 program package [18] and refined with SHELXTL-97 [19]. The most crystal data of complex **1** are listed in Table 1.

2.5. General procedure for the three component coupling reaction (A^3)

The coupling of benzaldehyde, piperidine and phenylacetylene with 1,4-dioxane as solvent was selected as a model reaction. The reaction was conducted by heating Eu(III) complex catalyst (70 mg), benzaldehyde (0.13 mmol), piperidine (0.15 mmol), and phenylacetylene (0.17 mmol) in 1,4-dioxane (1.5 g) without any additives or an inert atmosphere at 120 °C for 5 h. The yield of propargylamine is equal to the conversion of benzaldehyde, and was determined by using a by GC (GC1100, Capillary Column, SE-54) analysis.

3. Results and Discussion

3.1. Structural description

The complex **1** crystallizes in orthorhombic space group *FDD*2. The crystal structure of complex **1** is constructed by a central Eu(III) ion, two 4-imidazolecarboxaldehyde-pyridine-2-carbohydrazide anions, a isolated NO_3^- counter anion, four coordinated water molecules and four lattice water molecules (Figure 2). The Eu(III) ion is ten-coordinated with two oxygen atoms (O1 and O1A) of 4-imidazolecarboxaldehyde-pyridine-2-carbohydrazide ligand, four nitrogen atoms (N1, N1A, N3 and N3A) of 4-imidazolecarboxaldehyde-pyridine-2-carbohydrazide ligand, and four oxygen atoms (O1W, O1WA, O2W and O2WA) of coordinated water molecules.

There have four five-membered rings (ring 1: Eu1-O1-C5-N4-N3-Eu1, ring 2: Eu1-N1-C3-C4-N3-Eu1, ring3: Eu1-O1A-C5A-N4A-N3A-Eu1, ring 4: Eu1-N1A-C3A-C4A-N3A-Eu1) around central Eu(III) ion. The dihedral angles are 0.7° (ring 1 and ring 2), 4.2° (pyridine ring and imidazole ring), 1.6° (ring 1 and imidazole ring), 3.3° (ring 1 and pyridine ring), 3.9° (ring 2 and pyridine ring), 1.0° (ring 2 and imidazole ring), respectively. Which show that the molecule is almost coplanar. The bond lengths of Eu–O and Eu–N are accordance with those of reported in the literature [20].

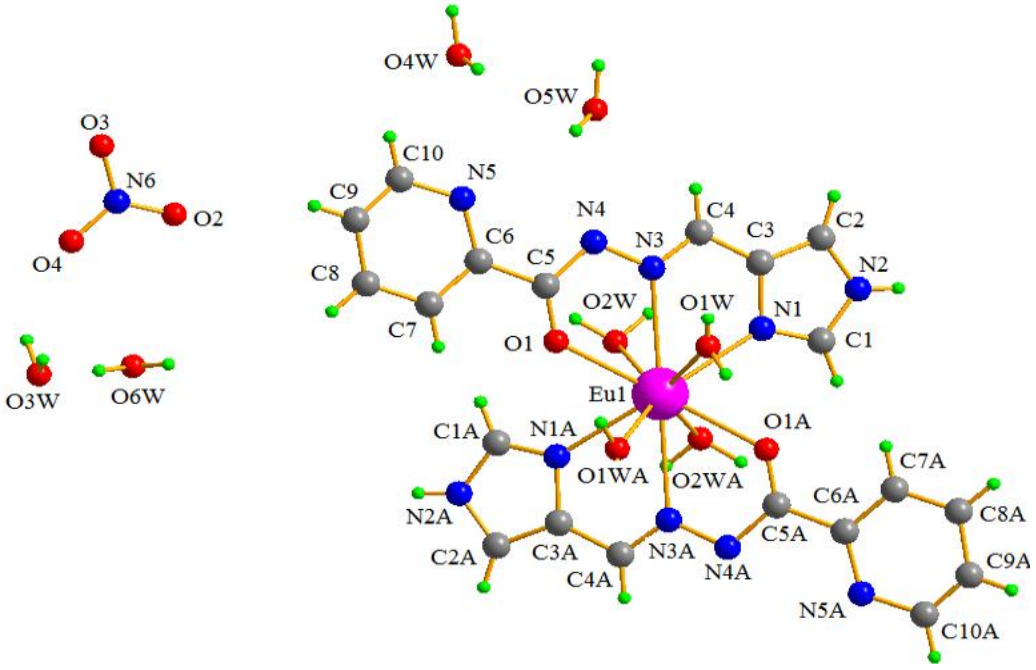

Figure 2. Molecular structure of complex **1**, symmetry code: *-x* + 3/2, *-y*-3/2, *z*

The complex molecules form 3D network structure by the aid of intermolecular hydrogen bonds and intramolecular hydrogen bonds (Table 2 and Figure 3).

Bonds for 1: Eu1-O2WA 2.479(6) Å; Eu1-O2W 2.479(6) Å; Eu1-O1WA 2.480(6) Å; Eu1-O1W 2.480(6) Å; Eu1-O1 2.512(7) Å; Eu1-O1A 2.512(7) Å; Eu1-N1A 2.575(8) Å; Eu1-N1 2.575(7) Å; Eu1-N3 2.698(5) Å; Eu1-N3A 2.698(5) Å; C5-O1 1.207(10) Å; O2-N6 1.239(11) Å; O3-N6 1.250(9) Å; O4-N6 1.242(10) Å; C1-N1 1.284(14) Å; C1-N3 1.417(11) Å; C1-N2 1.346(12) Å; N2-C2 1.356(12) Å; C4-N3 1.255(10) Å; N3-N4 1.365(9) Å; C5-N4 1.374(10) Å; N5-C6 1.372(12) Å; N5-C10 1.374(11) Å; C2-C3 1.394(12) Å; C3-C4 1.452(11) Å; C5-C6 1.507(10) Å; C6-C7 1.383(12) Å; C7-C8 1.387(14) Å; C8-C9 1.382(15) Å; C9-C10 1.272(14)Å.

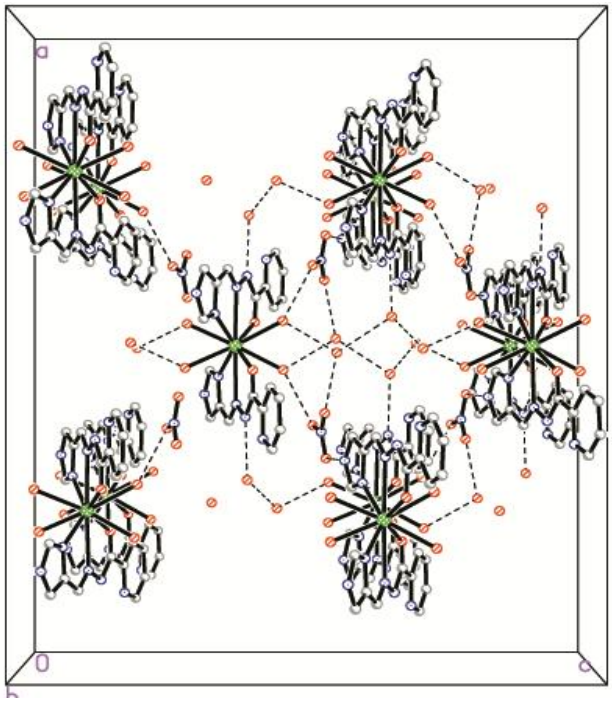

Figure 3. Packing of complex **1**

Angles for 1: O2W-Eu1-O2WA 65.1(3)°; O2WA-Eu1-O1WA 129.14(16)°; O2W-Eu1-O1WA 138.83(16)°; O2WA-Eu1-O1W 138.83(16)°; O2W-Eu1-O1W 129.14(16)°; O1W-Eu1-O1WA 69.6(3)°; O2WA-Eu1-O1 137.7(2)°; O2W-Eu1-O1 77.9(2)°; O1-Eu1-O1WA 69.2(2)°; O1-Eu1-O1W 80.7(2)°; O2WA-Eu1-O1A 77.9(2)°; O2W-Eu1-O1A 137.7(2)°; O1A-Eu1-O1WA 80.7(2)°; O1A-Eu1-O1W 69.2(2)°; O1A-Eu1-O1 143.3(3)°; N1A-Eu1-O2WA 77.7(2)°; N1A-Eu1-O2W 72.1(2)°; N1A-Eu1-O1WA 74.5(2)°; N1A-Eu1-O1W 140.7(2)°; N1A-Eu1-O1 71.8(2)°; N1A-Eu1-O1A 120.4(2)°; N1-Eu1-O2WA 72.1(2)°; N1-Eu1-O2W 77.7(2)°; N1-Eu1-O1WA 140.7(2)°; N1-Eu1-O1W 74.5(2)°; N1-Eu1-O1 120.5(2)°; N1-Eu1-O1A 71.8(2)°; N1-Eu1-N1A 144.1(4)°; N3-Eu1-O2WA 116.9(3)°; N3-Eu1-O2W 65.0(3)°; N3-Eu1-O1WA 113.8(3)°; N3-Eu1-O1W 64.4(3)°; N3-Eu1-O1 58.91(19)°; N3-Eu1-O1A 120.4(2)°; N3-Eu1-N1A 119.2(2)°; N3-Eu1-N1 61.5(2)°; N3A-Eu1-O2WA 65.0(3) °; N3A-Eu1-O2W 116.9(3)°; N3A-Eu1-O1WA 64.4(3)°; N3A-Eu1-O1W

Table 2. Hydrogen bonds for complex **1**

D-H…A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA
O1W-H1WB…O2	0.66	2.22	2.871(10)	171
O1W-H1WA…O4W	0.87	1.97	2.795(12)	159
N2-H2B…O3	0.86	2.04	2.896(10)	171
N2-H2B…O4	0.86	2.51	3.136(10)	130
O2W-H2WB…O2	0.96	2.43	3.044(10)	122
O2W-H2WB…O3	0.96	2.10	3.013(9)	159
O3W-H3WD…O2W	0.96	1.85	2.711(11)	148
O3W-H3WB…O5W	0.96	2.11	2.849(12)	132
O4W-H4WA…O5W	0.86	2.48	2.890(13)	110
O4W-H4WB…O5W	0.96	2.47	2.890(13)	106
O5W-H5WA…O3W	0.96	2.41	2.849(12)	107
O6W-H6WD…O3W	0.96	2.54	3.466(17)	163

113.8(3)°; N3A-Eu1-O1 120.4(2)°; N3A-Eu1-O1A 58.91(19)°; N3A-Eu1-N1A 61.5(2)°; N3A-Eu1-N1 119.2(2)°; N3A-Eu1-N3 178.0(6)°.

3.2. Catalytic studies

The prepared complex was used as a catalyst for A^3 coupling reaction of aldehyde, amine and terminal alkyne (Figure 4). The yield of propargylamine was determined by using GC (GC1100, Capillary Column, SE-54) analysis. The results exhibit that only a trace amount of propargylamine was obtained when do not use any catalyst. A yield of 2.8 % was obtained at 120 °C for 5 h. The yield of propargylamine was reached 16 % for 5 h at 120 °C using complex 1 as a catalyst. It can be seen that the complex has a higher yield of propargylamine than blank. However, the activity of complex is still less than those of Au/MOF and Cu(II) complex material [6,15].

3.3. Luminescent property

The luminescent properties of Eu(III) complexes have been received more interest because of their strong red luminescence emission [21]. Figure 5 displays the luminescence emission spectrum of complex **1** in solid state, it can be seen that the complex **1** gives two weak peaks (448 nm and 491 nm) and two strong peaks (596 nm and 620 nm) from excitation at 279 nm.

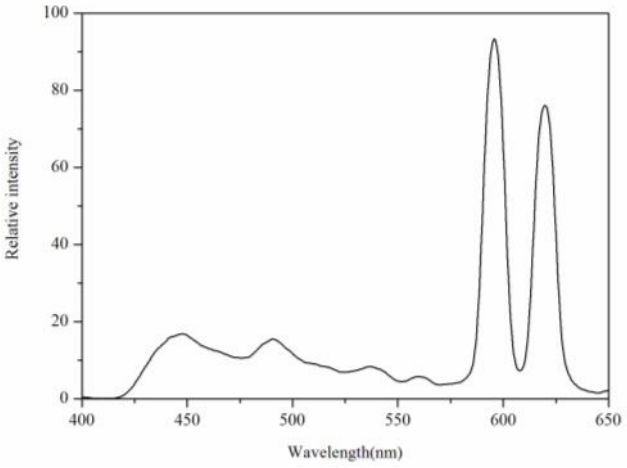

Figure 5. The emission spectrum of 1. The excitation and emission slit widths were 5 nm

4. Conclusions

In summary, a new Eu(III) complex has been synthesized and its structure has been determined by elemental analysis, IR, luminescent and X-ray single crystal diffraction analysis. The catalytic activity for A^3 coupling reaction using Eu(III) complex as catalyst is a higher yield of propargylamine than blank.

Acknowledgement

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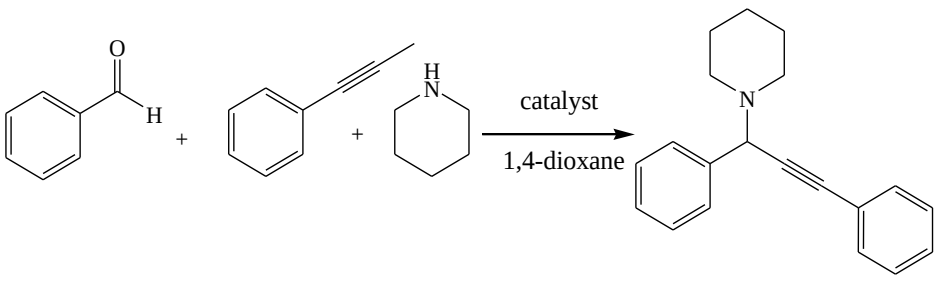

Figure 4. A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene using Eu(III) complex as catalyst

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